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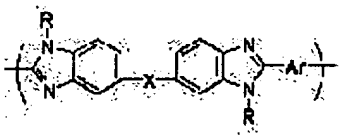
(54) SULFONIC ACID-CONTAINING ION CONDUCTIVE POLYBENZIMIDAZOLE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polymeric material which enhances the proton conductivity of a polybenzimidazole based polymer having a sulfonic acid group on the aromatic ring and excellent properties such as heat resistance and mechanical properties and, simultaneously, has sufficient water resistance when used as a polymeric electrolyte membrane.

SOLUTION: The sulfonic acid group-containing polybenzimidazole compound has a polymer composed of a repeating unit to be represented by formula (1) [wherein X is selected from -O-, -SO2-, -C(CH3)2-, -C(CF3)2-, -OPhO-, and a direct bond; Ar is selected from aromatic groups containing 0-2 sulfonic groups and contains an average of 0.5 per Ar of the sulfonic acid group; and R is selected from hydrogen, a 2-12C aliphatic group, an aromatic group, an aliphatic/ aromatic substituent, a 2-12C aliphatic sulfonic acid group, an aromatic sulfonic acid group, and an aliphatic/aromatic sulfonic acid substituent] as the major component, has an



(式1)

inherent viscosity, measured in sulfuric acid, of ≥0.1 and, simultaneously, is substantially insoluble in water.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

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[Date of extinction of right]

* NOTICES *

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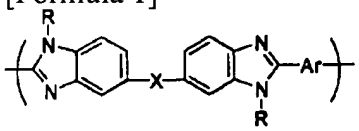
CLAIMS

[Claim(s)]
[Claim 1] the logarithm which used as the principal component the polymer which consists of a repeat unit expressed with the following general formula (1), and was measured in the sulfuric acid -- the sulfonic group content polybenzimidazole compound characterized by not dissolving in water substantially while viscosity is 0.1 or more.
[Formula 1]



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(X is chosen from -O-, -SO2-, -C(CH3)2-, -C(CF3)2-, -OPhO-, and direct coupling among a formula.) Ar is chosen from the aromatic series radical containing 0-2 sulfonic groups, and 0.5 or more sulfonic groups per Ar are contained as the average. R is chosen from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical and the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent.
[Claim 2] The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical in claim 1.
[Claim 3] The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent in claim 1.
[Claim 4] The moldings characterized by using a compound according to claim 1 to 3 as a principal component.
[Claim 5] Film characterized by using a compound according to claim 1 to 4 as a principal component.

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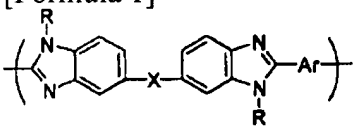

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to sulfonic group content polybenzimidazole system resin useful as polyelectrolyte film.
[0002]
[Description of the Prior Art] A water electrolyzer and a fuel cell can be raised as an example of the electrochemical equipment which uses a solid polymer electrolyte as an ion conductor instead of a liquid electrolyte. The poly membrane used for these must be chemical, thermal, electrochemical, and dynamic sufficiently stable in proton conductivity as cation exchange membrane. For this reason, as what can carry out a rear-spring-supporter activity, the perfluorocarbon-sulfonic-acid film which mainly makes "Nafion (trademark)" by U.S. Du Pont the example of representation has been used for a long period of time. However, if it is going to operate on the conditions exceeding 100 degrees C, membranous water content will fall rapidly, and also it becomes remarkable [membranous softening]. For this reason, in the fuel cell used as a fuel, degradation by the methanol transparency in the film cannot start the methanol with which the future is expected, and sufficient engine performance cannot be demonstrated. Moreover, also in the fuel cell operated near 80 degree C by using as a fuel the hydrogen currently examined by the current Lord, it is pointed out as a failure of establishment of a fuel cell technique that membranous cost is too high.
[0003] In order to conquer such a fault, the polyelectrolyte film which introduced the sulfonic group into the aromatic series ring content polymer is examined variously. For example, they are what sulfonated the poly aryl ether sulfone (Journal of Membrane Science, 83, 211 (1993)), the thing (JP,6-93114,A) which sulfonated the polyether ether ketone, sulfonated polystyrene, etc. However, a desulfonation acid reaction tends to occur with an acid or heat, and the sulfonic group introduced on the ring by using a polymer as a raw material cannot be said to be enough [endurance] for using it as an electrolyte membrane for fuel cells.
[0004] It is possible that the polymer of aromatic series poly azole systems, such as polybenzimidazole, is known as a polymer of a high heatproof and high endurance, a sulfonic group is introduced into these polymers, and it uses for the above-mentioned object. As such polymer structure, about the polybenzimidazole containing a sulfonic acid Uno's and others J.Polym.Sci., Polym.Chem., 15, 3 in 1309 (1977), 3'-diaminobenzidine, 3 and 5-dicarboxy benzenesulfonic acid or 4, 6-dicarboxy - what is compounded from 1 and 3-benzene disulfon acid By USP-5312895, it is reported that it is 1, 2, 4, and 5-benzene tetramine which compounds 2 and 5-dicarboxy benzenesulfonic acid as a principal component. However, in these reports, it did not look back about the electrochemical property which sulfonic groups, such as an electrolyte membrane application, have. Therefore, while reconciling thermal resistance, solvent resistance, the mechanical property, and the ionic conduction property, the molecular design which also took workability into consideration further was what is inferior to one of properties at least it not being carried out but using it for the polyelectrolyte film.
[0005] It is reported in USP No. 5,525,436 that the polyelectrolyte film which is excellent in the proton

conductivity in the elevated temperature in it sinking a sulfuric acid and a phosphoric acid into polybenzimidazole that polybenzimidazole applies to the polyelectrolyte film on the other hand paying attention to the thermal resistance which it originally has, solvent resistance, a mechanical property, etc. is obtained. Moreover, that to which what is used as a polyelectrolyte by introducing a sulfonic group into polybenzimidazole introduces N-alkyl sulfonic acid into polybenzimidazole is reported by JP,9-73908,A, USP No. 4814399, etc. Moreover, in the collection of macromolecule debate summaries, 49, and P.3217 (2000), the polymer of the structure which also contains N-alkyl chain simultaneously is shown in order to improve the mechanical strength of N-alkyl sulfonic-acid content polybenzimidazole. Thus, the approach of using as N-alkyl sulfonic acid the attempt which is going to obtain the polyelectrolyte film by introducing a sulfonic group into polybenzimidazole is examined until now, and the examination by what introduced the direct sulfonic group on the aromatic series ring of polybenzimidazole has not been reported. Although the polymer by which the sulfonic group is introduced on the ring of polybenzimidazole with N-alkyl sulfonic-acid structure is reported to USP5,312,876, since the polymer itself is water solubility and it cannot be used from the first as proton conductivity polyelectrolyte film used under moisture existence, the property as polyelectrolyte film is not evaluated in this system.

[0006] As mentioned above, in spite of having expected to excel in the thermal stability higher than other sulfonation poly arylene ether etc. for whether your being Haruka as the sulfonic acid introduced on the ring of polybenzimidazole was shown in J.Polym.Sci., Polym.Chem., 15, and 1309 (1977), it did not inquire in detail as polyelectrolyte film. This reason is considered to be because for it to be restricted in the conductivity of a proton also in electric field in order that the imidazole ring which mainly has the description as the sulfonic group and basic group on a ring may carry out salt formation between intramolecular or a molecule.

[0007]

[Problem(s) to be Solved by the Invention] In case it is simultaneously used as polyelectrolyte film, the object of this invention is to obtain polymeric materials with sufficient water resisting property, while raising the proton conductivity of the polybenzimidazole system polymer which has a sulfonic group on a ring with the property excellent in thermal resistance, a mechanical characteristic, etc.

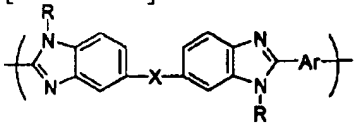
[0008]

[Means for Solving the Problem] In order to attain the above-mentioned object, as a result of repeating research wholeheartedly, this invention persons can improve a proton conduction property, maintaining a water resisting property by changing the imidazole ring top hydrogen of the polybenzimidazole system polymer containing a specific sulfonic group into a carbon system substituent, and came to get polymeric materials useful as polyelectrolyte film used for a fuel cell etc.

[0009] That is, this invention is attained by following the (1) - (5).

(1) the logarithm which used as the principal component the polymer which consists of a repeat unit expressed with the following general formula (1), and was measured in the sulfuric acid -- the sulfonic group content polybenzimidazole compound characterized by not dissolving in water substantially while viscosity is 0.1 or more.

[Formula 2]



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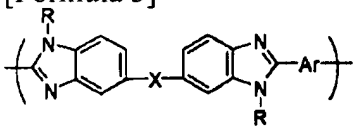
[0010] (2) The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series of 2-12 carbon numbers, aromatic series, aliphatic series / aromatic substitution radical in the general formula (1) under above (1).
[0011] (3) The sulfonic group content polybenzimidazole compound characterized by choosing R from hydrogen, the aliphatic series sulfonic acid of 2-12 carbon numbers, an aromatic series sulfonic acid, and aliphatic series / aromatic series sulfonic-acid substituent in the general formula (1) under above (1).
[0012] (4) The moldings characterized by using the above (1) thru/or the sulfonic group content polybenzimidazole compound in (3) as a principal component.
[0013] (5) Film characterized by using the above (1) thru/or the sulfonic group content polybenzimidazole compound in (4) as a principal component.
[0014]
[Embodiment of the Invention] This invention is explained to a detail below. With the sulfonic group content polybenzimidazole compound characterized by this invention using as a principal component the polymer which consists of a repeat unit expressed with the following general formula (1) and the moldings which makes it a principal component, and the film, while excelling in thermal resistance and a mechanical characteristic, the ingredient used as the solid polymer electrolyte having sufficiently high proton conductivity is offered. that logarithm measured in the sulfuric acid in order to use this resin constituent as a polyelectrolyte ingredient -- while viscosity is 0.1 or more, it is necessary not to dissolve in water substantially. a logarithm -- when viscosity is lower than this, problems, like handling becomes difficult arise.
[0015]
[Formula 3]



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[0016] The sulfonic group content polybenzimidazole compound shown by the above-mentioned general formula (1) is the approach which is indicated by JP,9-73908,A and USP No. 4814399 to the polybenzimidazole which has a sulfonic group on a ring, and after it transposes imidazole ring nitrogen top hydrogen to Na, Li, etc., it can be obtained by making it react with alkyl bromide and ape tons. As R in the above-mentioned formula (1), specifically A methyl group, an ethyl group, n-propyl group, n-butyl, n-pentyl radical, n-hexyl group, n-heptyl radical, n-octyl radical, n-nonyl radical, n-decyl group, n-undecyl radical, Straight chain alkyl groups, such as n-dodecyl, an isopropyl group, an isobutyl radical, 2-methylpropyl radical, sec-butyl, tert-butyl, an isopentyl radical, Although aliphatic series / aromatic substitution radicals, such as aromatic series radicals, such as branch-type alkyl groups including an iso hexyl group and 2-methyl pentyl radical, a phenyl group, a naphthyl group, and a toluyl radical, and benzyl, are raised, it is not limited to these. Moreover, some hydrogen atoms on these substituents may be changed by other substituents, such as a hydroxyl group and a halogen radical, and the element.